



Natural or fertilizer-derived uranium in irrigation drainage: a case study in southeastern Colorado, U.S.A.

R. A. Zielinski,* S. Asher-Bolinder, A. L. Meier, C. A. Johnson and B. J. Szabo

United States Geological Survey, Denver, CO 80225, U.S.A.

(Received 21 October 1995; accepted 9 March 1996)

Abstract—Drainage from heavily cultivated soils may be contaminated with U that is leached from the soil or added as a trace constituent of PO_4 -based commercial fertilizer. The effect of decades-long application of U-rich fertilizer on the U concentration of irrigation drainage was investigated in a small (14.2 km^2) drainage basin in southeastern Colorado. The basin was chosen because previous reports indicated locally anomalous concentrations of dissolved NO_3 ($6\text{--}36 \text{ mg l}^{-1}$) and dissolved U ($61 \text{ } \mu\text{g l}^{-1}$) at the mouth of the only stream. Results of this study indicated minimal impact of fertilizer-U compared to natural U leached from the local soils. Detailed sampling of the stream along a 6 mile (9.7 km) reach through heavily cultivated lands indicated marked decoupling of the buildup of dissolved NO_3 and U. Dissolved U increased markedly in the upstream half of the reach and correlated positively with increases in Na, Mg, SO_4 , B and Li derived from leaching of surrounding shaley soils. In contrast, major increases in dissolved NO_3 occurred farther downstream where stream water was heavily impacted by ground water return from extensively fertilized fields. Nitrogen isotopic measurements confirmed that dissolved NO_3 originated from fertilizer and soil organic N (crop waste). Uranium isotopic measurements of variably uraniferous waters showed little evidence of contamination with fertilizer-derived U of isotopically distinct $^{234}\text{U}/^{238}\text{U}$ alpha activity ratio (A.R. = 1.0). Leaching experiments using local alkaline soil, irrigation water and U-rich fertilizer confirmed the ready leachability of soil-bound U and the comparative immobility of U added with liquid fertilizer. Relatively insoluble precipitates containing Ca–P–U were formed by mixing liquid fertilizer with water containing abundant dissolved Ca. In the local soils soluble Ca is provided by dissolution of abundant gypsum. Similar studies are needed elsewhere because the mobility of fertilizer-derived U is dependent on fertilizer type, porewater chemistry and soil properties (pH, moisture, mineralogy, texture). © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

The impact of agricultural activity on water quality is an issue of growing global concern. Large tracts of land subjected to long-term cultivation act as non-point sources for a variety of contaminants including agricultural chemicals (pesticides, fertilizers), salts and toxic trace elements leached from soils. Nutrients and essential minerals present in fertilizer are also present in natural soils, and this fact complicates efforts to evaluate the impact of fertilizer application on the composition of irrigation drainage. Fertilizers have been identified as the most important source of dissolved NO_3 in agricultural areas, based largely on a combination of controlled field studies and multi-scale sampling tied to intensity of fertilizer use (see Alley, 1993; Spalding and Exner, 1993 for recent reviews).

Uranium is a trace constituent of many phosphate-bearing fertilizers, and the considerable enrichment of U in fertilizer compared to soils suggests that fertilizer could contribute measurable dissolved U to irrigation drainage. Reported U concentrations of $20\text{--}200 \text{ } \mu\text{g/g}$ in fertilizers correlate positively with percentage of P_2O_5 (Spalding and Sackett, 1972), and are comparable to the range of U concentrations found in phosphate rock from all major producing areas of

the world (Menzel, 1968). For comparison, the average crustal abundance of U is approximately $1 \text{ } \mu\text{g g}^{-1}$ (Taylor and McClennan, 1985). During manufacture of fertilizer from phosphate rock the original U is largely retained in superphosphate and phosphoric acid that are produced by acidulation or dissolution of phosphate rock with concentrated acids (Guimond and Windham, 1975; Roessler *et al.*, 1979).

Uranium is recognized by the World Health Organization (1993) as a potentially harmful constituent of drinking water and the U.S. Environmental Protection Agency (USEPA) has proposed to implement a drinking water quality standard of $20 \text{ } \mu\text{g l}^{-1}$ U by 1996 (U.S. Environmental Protection Agency, 1991). Concern over dissolved U is driven by numerous studies that demonstrate the chemical toxicity of U to the kidneys and by the potential for additional radiotoxicity effects in humans (Wrenn *et al.*, 1987).

In order to limit the amount of dissolved U contributed to water supplies from anthropogenic sources it is necessary to understand the effect of land use practices such as the application of U-bearing fertilizers. A few studies have attempted to document increased concentrations of U in upper portions of historically fertilized soil profiles (Rothbaum *et al.*, 1979) or in irrigation runoff or drainage from historically fertilized lands (Spalding and Sackett, 1972; Barisic *et al.*, 1992). These studies and a previous regional reconnaissance of dissolved U in the Arkan-

* Corresponding author.

sas River valley (Zielinski *et al.*, 1995) suggest that agricultural practices can elevate U concentrations in shallow soils and in co-existing water, but definitive linkage to fertilizer sources remains elusive. Interpretation of soil studies is complicated by large inventories of U in soil compared to applied U, variable natural concentrations of U in the soil, and probable differences in U mobility in different soil types and climatic settings. Apparent seasonal elevated concentrations of U in agricultural runoff or drainage cannot be definitively attributed to fertilizer because irrigation and/or spring runoff are often concurrent with fertilizer application and can promote enhanced leaching of natural U from soils.

In this study the possible linkage between fertilization and the concentration of dissolved U in surface water and shallow ground water was investigated at a field site where considerable spatial variation in dissolved U concentration could be related to differences in intensity of fertilization and to differences in concentration of dissolved NO_3 . In addition, the U isotopic composition of water samples was measured to look for evidence of isotopically distinct U that is derived from fertilizer. Finally, the leachability of fertilizer-hosted U was monitored in a laboratory experiment in which U-rich liquid fertilizer was applied to a constructed column of local, water-saturated soil. This combination of controlled field sampling, chemical and isotopic analysis, and controlled laboratory experiments provided a powerful methodology for evaluating the impact of fertilizer-U at the study site. The methodology should be directly applicable in other settings where fertilizer is a suspected source of dissolved U.

DESCRIPTION OF THE STUDY SITE

The study area is at approximately 1400 m elevation in the semi-arid High Plains of southeastern Colorado, along the valley of the Arkansas River (Fig. 1). Sampling is confined to the irrigated 5.5 mile² (14.2 km²) portion of the drainage basin of Sixmile Creek; a natural tributary of the Arkansas River that joins the river approximately 12 mile (19 km) east of Pueblo, Colorado (Fig. 1). The Sixmile Creek drainage was chosen for study because of its accessibility, small area, long history of agricultural development, and efficient drainage towards Sixmile Creek. In addition, previous sampling of water at the mouth of the creek indicated locally anomalous concentrations of dissolved NO_3 (6–36 mg l⁻¹, Cain and Edelmann, 1980; Cain, 1985) and dissolved uranium (61 µg l⁻¹, Zielinski *et al.*, 1995).

Sixmile Creek is a natural intermittent stream, but perennial flow is sustained in the final 6 mile (9.7 km) reach of the creek that extends from the point of the creek's intersection with Bessemer irrigation ditch to the Arkansas River (Fig. 2). Bessemer ditch diverts water from the Arkansas River at a site above Pueblo

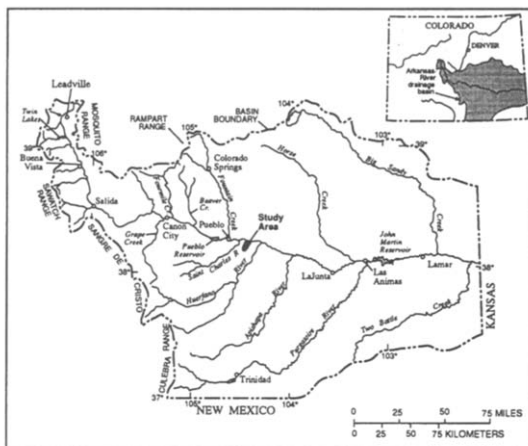


Fig. 1. Location of irrigated lands of the Sixmile Creek drainage, Arkansas River basin, southeastern Colorado.

presently occupied by Pueblo Reservoir (Fig. 1). The ditch is the major supply of irrigation water to the Sixmile Creek drainage and to an additional 8000 ha located south of the Arkansas River between Pueblo and the Huerfano River (Fig. 1; Abbott, 1985). Cultivated lands have been serviced by the Bessemer ditch for over 100 a.

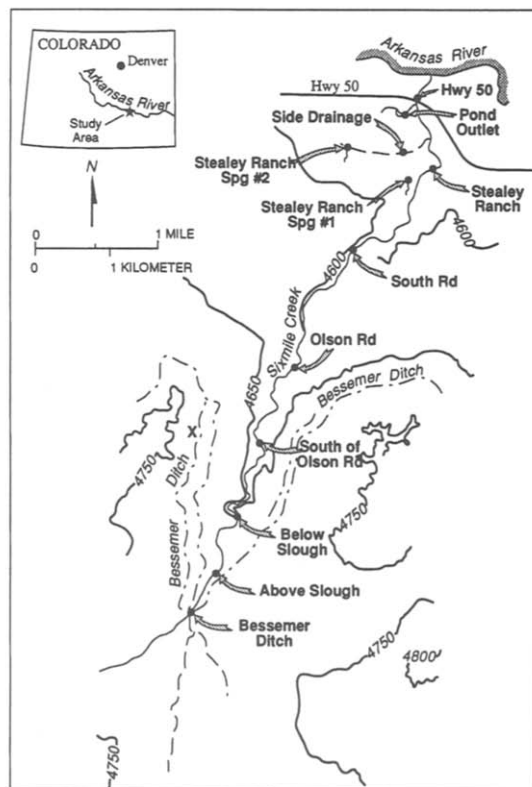


Fig. 2. Map of the study area. Selected contour intervals are in feet. Locations of water samples are indicated by labeled dots. The location of the soil sample used in the soil column experiment is indicated by an 'X'.

The irrigated portion of Sixmile Creek drainage is underlain by an erosional surface of Pierre Shale, a calcareous, sulfidic marine shale of Late Cretaceous age (Scott *et al.*, 1978). Present topography is the result of episodic lowering of base level and down-cutting of streams during Pleistocene and Holocene times. Erosional remnants of several gravel-capped terraces occur at closely spaced elevations above the Arkansas River. One of the younger alluvial gravels (Louviere Alluvium of Scott *et al.*, 1978) forms a thin (<2 m) cover over shale bedrock in most of the flat-lying irrigated lands between Bessemer Ditch and the Arkansas River. In other portions of the study area the shale is overlain by fine-grained colluvium and alluvium of Pleistocene and Holocene age that includes locally derived slopewash and windblown sand and silt.

Mapped soils (Ustic Torriorthents) in irrigated portions of the study area belong to the Rocky Ford Series and consist of immature, well-drained silty clay loams developed on alluvial terraces (Larsen *et al.*, 1979). The soil is alkaline, calcareous and typically shows some evidence of translocated soil carbonate at depth. Soils are poorly developed and B horizons are absent. Soil depth can be as much as 2 m. Outside of irrigated areas Manvel Series silt loams are developed on silty colluvial and alluvial material. Manvel soils are similar in most respects to Rocky Ford soils but are less permeable and somewhat more calcareous and saline (Larsen *et al.*, 1979).

In the Sixmile Creek drainage all irrigated agriculture is confined to lands situated between the Bessemer Ditch and the Arkansas River (Fig. 2). The ditch makes a sharp bend to the S to include gently sloping lands bordering a 3 mile reach of Sixmile Creek in a narrow valley between the Badger Hills (Fig. 2). The remaining 3 mile reach between Olson road and the Arkansas River receives drainage from a broader area of flatter lying land that comprises approximately 75% of the drainage basin. Irrigation is by periodic flooding, and irrigation-return flow consists of surface runoff (tailwater) and ground-water return. Irrigation water that percolates through the local well-drained soils enters underlying alluvial gravels. The relatively permeable gravels provide a suitable host for a shallow (<10 m) unconfined aquifer developed on weathered shale bedrock. The slope of the water-table mimics the local topography and this allows for efficient drainage of shallow ground water towards Sixmile Creek (Cain, 1985). Springs and seeps occur along the valley of the creek where erosion has exposed the shallow contact between shale bedrock and overlying sediments.

Major crops in the Sixmile Creek drainage include hay, corn, melons, onions, pinto beans and peppers. The irrigation season extends from April to October. Water use for row crops is intensive in this temperate semi-arid climate where mean pan evaporation is 3.5–5 times precipitation (U.S. Department of Commerce, 1991). Delivered ditch water is supplemented by

pumpage from a few shallow (<10 m) wells and from precipitation. Mean annual precipitation averages 12 in (30.5 cm) and about 75% occurs during the irrigation season (Mueller *et al.*, 1991).

The most intense application of fertilizers in the study area occurs in April in conjunction with planting and the beginning of irrigation. Crops with high demands for nutrients may receive an additional application during the early growing season. Local fertilizer usage is divided between anhydrous NH_3 (80% of total) and another liquid fertilizer of formulation 10-34-0 (total N, available P_2O_5 , soluble K_2O , in wt%). These liquid fertilizers, applied at rates of 200–400 lbs acre⁻¹ (37–74 kg ha⁻¹), are injected through tubes mounted behind blades of furrowers or are sprayed as side-dressing applications to young plants. The 10-34-0 fertilizer has been applied in the area for at least 20 a (M.C. Genova, American Fertilizer Company, oral communication) and is of particular interest because of its high PO_4 analysis and potential for high concentrations of contained U. The 10-34-0 fertilizer is a polyphosphate-rich synthetic fertilizer produced by reacting superphosphoric acid with NH_3 vapor (pipe process; Meline *et al.*, 1972). Phosphate rock that is dissolved in H_2SO_4 to produce the superphosphoric acid is from the highly uraniferous (100–200 $\mu\text{g g}^{-1}$) Phosphoria Formation of Idaho (McKelvey and Carswell, 1956; T. Broz, Kugler Company, oral communication, 1993).

SAMPLE COLLECTION, ANALYTICAL AND EXPERIMENTAL METHODS

Water and fertilizer samples

Surface water samples were collected on April 22–23, 1993 from Bessemer Ditch and from 7 locations along Sixmile Creek between Bessemer Ditch and the Arkansas River (Fig. 2). Additional samples included one seep, two springs, and outflow from a pond that collects irrigation runoff. The quantity and quality of these waters were assumed to represent normal early-irrigation season conditions in the drainage. The samples provided a relatively instantaneous snapshot of downstream changes in dissolved constituents caused by increasing water/soil interactions and inputs of irrigation drainage. Flow in Sixmile Creek was crudely estimated using observations of stream dimensions and flow velocity and fell within the range of 0.05 to 0.13 m³ s⁻¹ reported by Cain and Edelmann (1980). Three additional samples of surface runoff from irrigated fields were collected to compare to Bessemer Ditch water (BDW).

The specific conductance, temperature and pH of water samples were measured *in situ*. Samples of 125 ml were filtered through 0.45 μm membranes at the time of collection and placed under refrigeration. Upon return to the laboratory, alkalinity (as HCO_3^-) was determined by titration with standard acid. A

20 ml aliquot was retained for determination of other anions (Cl , SO_4 , NO_3) by ion chromatography (IC), and the remainder was acidified to $\text{pH} < 2$ with ultrapure grade HNO_3 and analysed for dissolved U by inductively coupled plasma-mass spectrometry (ICP-MS), and for dissolved silica and dissolved cations by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Analytical precision and accuracy were estimated based on replicate analyses of prepared standards and are better than $\pm 10\%$ (relative standard deviation) for the reported elements. The analytical detection limit for dissolved U was $0.1 \mu\text{g l}^{-1}$.

Based on the concentrations of dissolved U and NO_3 measured in April, several of the sample sites were selected for resampling in August in order to collect larger volumes (1–10 l) of filtered water for U and N isotopic analyses. For U isotope measurements, a spike of ^{236}U was added to each sample and dissolved U was scavenged from solution by coprecipitation with Fe hydroxide. The recovered precipitate was dissolved in acid and processed with a series of anion-exchange resins to purify the U. Dissolved U was then electro-deposited as a thin film on a stainless steel planchet. Alpha activities of U isotopes were determined by alpha spectrometry (Rosholt, 1984). A minimum of 10 000 counts was accumulated at each alpha energy peak of interest. Precision of the reported $^{234}\text{U}/^{238}\text{U}$ alpha activity ratios (A.R.) is better than $\pm 2\%$ (relative standard deviation) and is based on the average determination from two separate counting periods.

Nitrate-N was separated from water samples by steam distillation. Distillates were evaporated to dryness, combusted to form N_2 gas, and admitted to a mass spectrometer for N isotopic determination (Kendall and Grim, 1990; Johnson *et al.*, 1995). Nitrogen isotopic composition is reported in terms of a $\delta^{15}\text{N}$ -value, where:

$$\delta^{15}\text{N}(\text{‰}) = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000$$

R is the atomic $^{15}\text{N}/^{14}\text{N}$ ratio and the standard is atmospheric N_2 . Reported $\delta^{15}\text{N}$ values are the average of at least two distillations and have an estimated one sigma precision of ± 0.4 permil, based on repeated analysis of a standard solution.

Samples of 10-34-0 liquid fertilizer were obtained from the local supplier in April and August. Uranium concentrations and U and N isotopic compositions were determined on diluted fertilizer solutions as described for water samples. For fertilizer samples the original N is present as NH_4 .

Soil samples

Approximately 2 kg of local soil was collected for use in the soil column experiment. A composite sample was collected from depths of 10–30 cm at a

site in the W-central part of the study area, just W of the Bessemer ditch (Fig. 2). The site was chosen because the local Manvel Series soil is compositionally similar to soils in the irrigated lands but is not irrigated or fertilized. Use of unfertilized soil in the soil column experiment simplified interpretation of the effects of controlled addition of 10-34-0 fertilizer. The soil sample was air-dried, gently disaggregated with a ceramic mortar and sieved to remove the few rock fragments larger than 2 mm in diameter. A split of the sieved soil was retained for grain-size analysis and mineralogical observations (optical and X-ray diffraction) and the remainder was stored separately for use in the soil column experiment.

Soil column experiment

The soil column experiment was contained in a clear acrylic cylinder, 8.6 cm diameter \times 22 cm high, that is part of a commercial 'barrel filter' apparatus designed for pressure filtration of water samples (Geotech Inc., Denver, CO). Large O-rings at each end of the cylinder provide a water tight seal when acrylic endplates are attached. The upper endplate contains an inlet-port nipple fitting for attaching tubing to deliver pressurized gas. The lower endplate has an outlet port and is designed to hold a nylon filter support and 103 mm diameter filter paper. The apparatus was assembled with a $0.45 \mu\text{m}$ filter membrane of cellulose acetate in the lower endplate. Quartz sand was added to a depth of 1 cm to provide a prefilter medium, and the sand was rinsed by passing 1 l of distilled water.

Approximately 1.3 kg of sieved soil was combined with 500 ml of Bessemer Ditch water (BDW) to produce a soil saturation paste. This slurry was allowed to stand for several days with periodic stirring. The prepared soil/water mixture was added in increments as a stirred slurry to the column. The soil column was packed to an initial height of approximately 15 cm as determined by initial settling of the added slurry. The slurry was restirred and allowed to stand with the outlet port plugged. After one week any floating organic matter was removed from the standing water and approximately 100 ml of BDW was allowed to pass the column.

One ml of 10-34-0 liquid fertilizer was added to a thin film of standing water above the soil column and allowed to percolate onto the soil as the column drained. This was followed by 3 successive applications of 5 ml BDW and finally 300 ml of BDW. After addition of the large volume of BDW the upper endplate was attached and sufficient pressure from N_2 gas (15–25 psi) was applied to maintain an elution rate of 10 ml h^{-1} . This elution rate is 10–30% of that predicted based on permeability measurements of Rocky Ford Series clay-loams (L. Sutherland, U.S. Dept. of Agriculture, written communication, 1996). Eluted solutions were collected in 20 ml fractions in

polyethylene scintillation vials. Sixty fractions were collected during workdays over a period of 3–4 weeks. The reservoir of standing BDW was periodically replenished and the water level was never allowed to drop below the water/soil interface. Each collected fraction was checked for specific conductance and analysed for dissolved U (ICP-MS), dissolved PO_4 , Cl, SO_4 and NO_3 (IC) and dissolved NH_3 . The latter was determined on a 1:5 dilution using a colorimetric method based on reaction with Nessler reagent (K_2HgI_4 ; Hach Company, 1992).

At the end of the experiment the column of moist soil had settled to a height of 12 cm. The moist soil was carefully excavated by scraping successive cm-thick layers from the surface with a metal spatula. Individual layers were dried, weighed, and splits were submitted for U and Th analysis by a delayed neutron activation technique (Millard and Keaten, 1982). Results have an estimated precision of better than 2% for U and 10% for Th (relative standard deviation).

Other experiments

Additional experiments were performed to observe the effect of combining 1 ml of 10-34-0 liquid fertilizer with 20 ml of BDW or with dilute solutions of a variety of soluble salts (NaCl , CaCl_2 , MgCl_2 , Na_2SO_4 , CaSO_4). In some cases a white precipitate formed and a sample of one such precipitate was prepared in larger quantities. The precipitate was investigated by X-ray diffraction and submitted for chemical analysis of U by delayed neutron activation, C-H-N by combustion gas chromatography, and other major and trace elements by ICP-AES.

RESULTS AND DISCUSSION

Water chemistry

Bessemer Ditch water that is diverted to sustain flow in Sixmile Creek or that is applied as irrigation water to surrounding fields undergoes dramatic changes in chemical composition through soil–water interaction. These changes are indicated by downstream evolution of the composition of Sixmile Creek and by the composition of shallow ground water (Tables 1 and 2). The concentration of U and of most other dissolved constituents increased by factors of 2–13 in the first 2 miles (3.2 km) of the stream below Bessemer Ditch (SM-6; Table 1). The most dramatic increases were for SO_4 (13 \times), U and Mg (9 \times), Sr (8 \times), Na and Ca (6 \times). Other water parameters such as specific conductance and total dissolved solids necessarily increased as well. Farther downstream the concentrations of most dissolved constituents were much less variable and fluctuated about the values observed at the 2 mile location, suggesting

some adjustment to local ambient conditions. Dissolved concentrations at Hwy 50 (SM-15) were lower than at upstream locations and were influenced by outflow from a nearby pond (SM-14) that collects both tailwater and ground-water return. Temporal variability of creekwater composition was not investigated in this study but the measured composition at Hwy 50 is generally within the range of compositions reported for samples collected at the mouth of the creek during the 1976 and 1978 irrigation seasons (Table 1; Cain and Edelmann, 1980).

Dissolved U concentrations of 36–46 $\mu\text{g l}^{-1}$ in the lower portion of Sixmile Creek greatly exceeded the USEPA-proposed Maximum Contaminant Level (MCL) of 20 $\mu\text{g l}^{-1}$ and were high compared to reported concentrations of 10–15 $\mu\text{g l}^{-1}$ in nearby locations along the Arkansas River (Zielinski *et al.*, 1995). The solubility of U in Sixmile Creek and in other surface waters of the region is enhanced by alkaline pH and sufficient dissolved oxygen to stabilize U as highly soluble U(VI) species. Dissolved O_2 concentrations in Sixmile Creek were measured during the August sampling and ranged from 6 to 11 mg l^{-1} , in agreement with the 7–12 mg l^{-1} range reported by Cain (1985) at the Hwy 50 site. Spring waters were slightly less oxygenated at 3–7 mg l^{-1} . Speciation of dissolved U was calculated with the computer code PHREEQE (Parkhurst *et al.*, 1980) and utilized a thermodynamic database for dissolved U species and U minerals from Langmuir (1978). Results indicated that uranyl di- and tri-carbonate species account for >85% of the dissolved inorganic U species under oxidizing conditions ($E_h = 0.4$ V). Similarly elevated concentrations of U in ground water of Sixmile drainage (16–48 $\mu\text{g l}^{-1}$) suggests that the shallow unconfined aquifer does not sustain sufficiently reducing conditions ($E_h < 0.1$ V) to permit precipitation of relatively insoluble U(IV) minerals such as uraninite or coffinite.

Dissolved U had a large positive correlation ($r > 0.70$) with several other readily soluble constituents Na, Mg, SO_4 , B and Li (Fig. 3). These constituents are dissolved as irrigation water or precipitation and interact with the local calcareous marine shale and derivative soils. Shale and shaley soils of the area provide dissolved solids primarily through dissolution of sparingly soluble gypsum and through ion-exchange reactions involving clay minerals. Evaporation of water allows for temporary storage of dissolved solids in the form of highly soluble Na- and (Na, Mg)- SO_4 salts that form white efflorescent crusts on surfaces of poorly drained soils (Zielinski *et al.*, 1995). Equilibrium-based mineral solubility calculations with PHREEQE confirmed that BDW and the other analysed waters are undersaturated with gypsum and other soluble SO_4 salts such as thenardite and mirabilite. In contrast, the same waters are oversaturated with quartz, calcite, dolomite, and Fe^{3+} oxides ($E_h > 0.1$ V), indicating that these phases are much less likely to act as major sources of dissolved solids under

Table 1. Chemistry of water collected from Bessemer ditch and Sixmile Creek, April, 1993

Sample no. Sample site	SM-1 Bessemer Ditch	SM-2 Above Slough	SM-3 Below Slough	SM-6 South of Olson Rd	SM-7 Olson Rd	SM-8 South Rd	SM-10 Stealey Ranch	SM-15 At Hwy 50	Previous* at mouth (n = 6 to 14)
Downstream mile		0.37	0.97	1.94	2.77	3.97	5.01	5.84	5.84
Major chemical constituents (mg l ⁻¹)									
SiO ₂	8.6	17.1	21.4	21.4	19.3	19.3	19.3	17.1	16–23
Na	21	65	120	130	140	120	120	93	110–140
K	3	2	2	5	4	4	4	4	
Ca	56	210	340	340	360	320	350	280	300–390
Mg	16	44	94	140	160	120	120	89	110–140
Fe	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	
HCO ₃	145	188	233	233	190	225	250	270	234–287
SO ₄	127	625	1240	1634	1910	1450	1590	1100	1100–1500
Cl	8	31	40	21	30	24	25	24	9–32
NO ₃	0.6	0.85	0.2	1.2	0.35	9.3	36	58	6–36
Additional parameters									
Total diss. solids (mg/l)	304	1073	1956	2391	2703	2163	2373	1785	1780–2352
T °C	10	10	9.5	18	19	19	18	15	14–27.5
Specific conductance (µS/cm)	560	2000	2900	2700	3200	2500	3000	2400	1850–2850
pH	8.35	7.85	7.80	8.35	8.25	8.10	7.85	8.05	7.9–8.4
Minor and trace constituents (µg l ⁻¹)									
Mn		<40	210	530	130	69	58	<40	<40
Sr		630	2900	5200	4900	5200	4600	5100	4100
Ba		61	53	55	38	29	43	32	37
Li		<50	<50	80	130	170	130	120	87
B		<50	82	180	320	350	320	350	290
U		5.0	9.6	16	45	46	38	39	36

* Range of values reported for 14 samples collected during the irrigation seasons of 1976, 1978 (Cain and Edelmann, 1980). Other constituents sought but below the level of detection (µg l⁻¹) include Ag(20), Al(500), Be(20), Cd(20), Co(40), Cr(40), Cu(80), Ga(100), Mo(80), Ni(80), P(100), Pb(100), Sn(100), Ti(200), V(40), Zn(40), Zr(40).

Table 2. Chemistry of other waters collected in the Sixmile Creek drainage

Sample no. Sample Site	SM-3A Seep near Sample SM-3	SM-9 Spring 1 at Stealey Ranch	SM-12 Spring 2 at Stealey Ranch	SM-14 pond outlet
Major chemical constituents (mg l ⁻¹)				
SiO ₂	21.4	23.6	21.4	17.1
Na	29	91	100	85
K	<1	3	3	3
Ca	580	350	310	230
Mg	36	84	96	81
Fe	<0.5	<0.5	<0.5	<0.5
HCO ₃	353	280	303	288
SO ₄	1246	1230	1200	1020
Cl	15	18	33	25
NO ₃	<0.1	95	100	90
Additional parameters				
Total diss. solids (mg l ⁻¹)	2089	2015	1996	1680
T °C	11	13	11.5	13
Specific conductance (µS cm ⁻¹)	3400	2500	2600	2200
pH	7.40	7.30	7.25	7.90
Minor and trace constituents (µg l ⁻¹)				
Mn	630	<40	<40	<40
Sr	7600	5500	4700	3700
Ba	<20	<20	21	41
Li	<50	84	86	71
B	71	280	320	270
U	15	38	48	32

Other elements sought but below detection limits are the same as in Table 1.

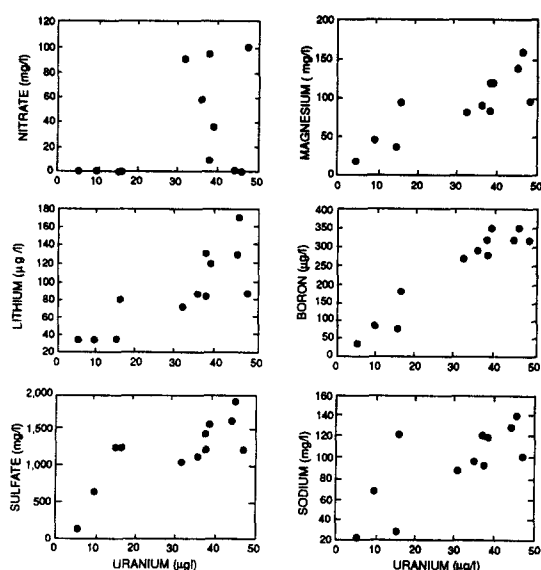


Fig. 3. Correlation plots of dissolved U versus other dissolved constituents in 12 water samples collected in the drainage of Sixmile Creek, east of Pueblo, Colorado.

equilibrium conditions. Similarly, sensitivity calculations indicated that clay minerals, feldspar and illite are oversaturated in these waters when dissolved Al concentrations exceed $10 \mu\text{g l}^{-1}$. Waters are undersaturated with amorphous silica which could provide a source of dissolved silica.

The synoptic sampling of this study indicated that the majority of NO_3 contamination occurs in the lowest 3 mile (4.8 km) reach of Sixmile Creek (Table 1). This reach receives subsurface drainage from the majority of irrigated and fertilized lands in the Sixmile Creek basin. In April, 1993 dissolved NO_3 concentrations in Sixmile Creek below Olson Road ($9\text{--}58 \text{ mg l}^{-1}$) and in springs and a tributary along the same reach ($58\text{--}100 \text{ mg l}^{-1}$) approached or exceeded the existing USEPA Maximum Contaminant Level of 44 mg l^{-1} ($10 \text{ mg l}^{-1} \text{ N-NO}_3$). Concentrations of this magnitude clearly exceed the commonly suggested threshold concentration of 13 mg l^{-1} ($3 \text{ mg l}^{-1} \text{ N-NO}_3$) for naturally-sourced NO_3 in ground water (Madison and Brunett, 1985). Fourteen water samples collected at the mouth of Sixmile Creek in 1976 and 1978 ranged from 6 to 36 mg l^{-1} total nitrate (Cain and Edelmann, 1980; Cain, 1985). These concentrations were anomalous compared to the adjacent Arkansas River but were similar to concentrations found in some engineered irrigation-return drains farther downriver. In contrast to dissolved NO_3 , total orthophosphate was barely detectable ($<0.01\text{--}0.02 \text{ mg l}^{-1}$) in their samples.

Water collected near the mouth of Sixmile Creek (SM-15) was anomalously concentrated in U as well as NO_3 , but the more detailed sampling of this study indicated that, in contrast to NO_3 , the majority of U enrichment occurred in the upper portion of the creek (Table 1; Fig. 4). In this regard U more closely

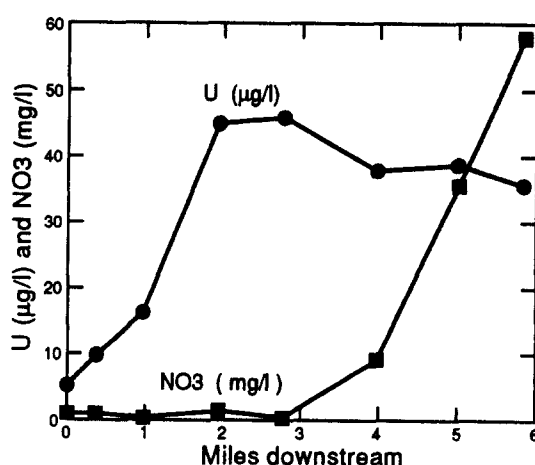


Fig. 4. Concentrations of dissolved U and dissolved NO_3 in Sixmile Creek, plotted as a function of distance downstream from Bessemer ditch. The composition of Bessemer ditch water is plotted on the ordinate for comparison.

paralleled the behavior of other dissolved constituents that are provided by natural water-rock interactions. The strong spatial decoupling between U and NO_3 explains the poor correlation between these two highly soluble constituents (Fig. 3). Concentrations of dissolved U in the lower portion of Sixmile Creek were stable or slightly decreasing compared to peak values at the 2-mile (3.2-km) mark. This suggests that NO_3 -rich drainage is not enriched in U compared to ambient concentrations already established in the upstream portion of the creek.

Nitrogen isotopes

The N-isotopic compositions of NO_3 -rich waters from lower Sixmile Creek drainage were measured to compare with the isotopic signature of locally applied fertilizer (Johnson *et al.*, 1995). Similarities in isotopic composition could be used to confirm a fertilizer source directly, whereas differences in composition could indicate other sources, or processes acting to modify the isotopic composition of fertilizer N between the time of application (as NH_3) and collection as geologically well-travelled NO_3 .

The N-isotopic signature of commercial chemical fertilizer is quite uniform because the contained N is derived from air, and incorporation in fertilizer produces minimal isotopic fractionation. Atmospheric N_2 is the standard against which N-isotopic measurements are compared, so fertilizer products have $\delta^{15}\text{N}$ -values that cluster tightly about a mean value of $0 \pm 4\text{‰}$ (Heaton, 1986). Two samples of 10-34-0 liquid fertilizer had $\delta^{15}\text{N}$ values analytically indistinguishable from 0 (Table 3). Three samples of surface water collected in August, 1993 from the lower portion of Sixmile Creek had $\delta^{15}\text{N}$ values that increased from -1.8 to 1.6 with progressive distance downstream, but all fell within a range consistent with

Table 3. Nitrate concentration and N isotopic composition of water from the Sixmile Creek drainage collected August, 1993, and in 10-34-0 liquid fertilizer

Sample	NO ₃ (mg l ⁻¹)	δ ¹⁵ N _{AIR} (‰)	Comments
Sixmile Creek at South Rd	12	-1.8	SM-8 revisited
Spring 1 at Stealey Ranch	71	3.6	SM-9 revisited
Spring 2 at Stealey Ranch	106	5.6	SM-12 revisited
Sixmile Creek at Stealey Ranch	9*	0.7	SM-10 revisited
Pond outlet	39	4.4	SM-14 revisited
Sixmile Creek at Hwy 50	15*	1.6	SM-15 revisited
Side drainage, Stealey Ranch	128	4.0	New site, spring-fed
	NH ₄ ⁺ (mg l ⁻¹)		
10-34-0 liquid fertilizer	major	-0.2	Sampled 4/93
10-34-0 liquid fertilizer	major	0.1	Sampled 8/93

* Concentration values lower than expected because of heavy rains the night before collection.

a fertilizer source (Table 3). For comparison, other possible sources of local NO₃ contamination such as animal or sewage waste should generate isotopically heavy NO₃ with δ¹⁵N > 10‰ (Heaton, 1986).

Two NO₃-rich springs, a spring-fed tributary to Sixmile Creek, and outflow from a pond that is partially sustained by spring water all had δ¹⁵N values between 3.6 and 6.0‰ (Table 3). These values are distinctly heavier than applied fertilizer and fall within the range of 4–8‰ that is typical for soil organic N (Heaton, 1986). Crop waste is the major source of soil organics in the irrigated areas and is an obvious sink for N. Mineralization of crop waste converts organic-N to NO₃ and releases abundant NO₃ of isotopically heavy composition to local ground water (Heaton, 1986). Bacterially mediated denitrification is an alternative process that can also produce isotopically heavy NO₃. This process converts dissolved NO₃ to N₂ gas under anoxic conditions and has been documented in previous studies of aquifers similar to those underlying the Sixmile Creek drainage (Trudell *et al.*, 1986). Denitrification is characterized by a large kinetic isotope fractionation of some 25 to 35‰ (Heaton, 1986). Because of the large fractionation, a NO₃ loss of some 15% is sufficient to increase the δ¹⁵N value of the remaining NO₃ to the 5–6‰ range.

In Sixmile Creek the downstream trend towards isotopically heavier values is consistent with increased input from ground water sources such as the NO₃-rich springs. A plot of δ¹⁵N values versus dissolved NO₃ shows that surface and ground water samples lie along a hyperbola that, in this type of plot, defines a mixing relationship between low-NO₃, fertilizer-like water (runoff or short-residence ground water) and high-NO₃, isotopically heavier ground water of δ¹⁵N = 5‰ (Fig. 5).

Uranium isotopes

The U isotopic compositions of 10 water samples from the Sixmile drainage were measured to look for

evidence of contamination by fertilizer-U. As mentioned above, most PO₄-based fertilizers have high concentrations of U compared to most rocks and soils. In addition these fertilizers have distinctive ²³⁴U/²³⁸U alpha activity ratios (A.R.) of approximately 1.0 which signifies close approach to radioactive equilibrium (Guimond and Windham, 1975; Mangini *et al.*, 1979). The A.R. of approximately 1.0 is inherited from the original phosphate ore because acidulation or dissolution of phosphate rock by concentrated acid causes minimal isotopic fractionation. The original phosphate rock is in radioactive equilibrium because the relatively insoluble, uraniferous apatite behaves as a natural closed system that is disturbed only under conditions of extreme weathering. Two samples of 10-34-0 liquid fertilizer contained 100 and 34 µg ml⁻¹ U, respectively, with

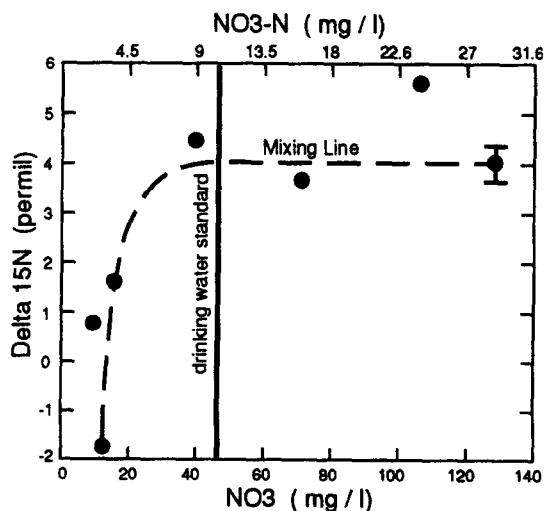


Fig. 5. Nitrogen isotopic composition plotted versus NO₃ concentration for NO₃-rich water samples from the drainage of Sixmile Creek. The USEPA drinking water quality standard is plotted for reference. On this diagram samples that approximate two-component mixtures lie along an hyperbola connecting endmember components. The vertical error bar is the estimated standard deviation of N-isotopic values, based on replicate determinations.

$^{234}\text{U}/^{238}\text{U}$ activity ratios analytically indistinguishable from 1.0 (Table 4).

The rock-like A.R. of fertilizer contrasts with the A.R. values of most natural waters which are typically >1.0 (Osmond and Cowart, 1982; Scott, 1982). Selective enrichment of ^{234}U in most natural waters is the result of preferential leaching and decay-induced recoil of ^{234}U daughter from sparingly soluble sites on mineral surfaces. Five water samples collected along the Arkansas River in Colorado during the summer of 1983 had A.R. values ranging from 1.21 to 1.59 (Kuroda *et al.*, 1989). Waters from Sixmile drainage collected in August, 1993 had $^{234}\text{U}/^{238}\text{U}$ alpha activity ratios in the range of 1.26 to 1.55 (Table 4).

A plot of A.R. versus $1/\text{U}$ shows that surface and ground waters lie along a visually fitted sloping line that, in this type of plot, defines a mixing relationship between low-U Bessemer Ditch water (A.R. = 1.55) and high-U ground water samples of A.R. near 1.26 (Fig. 6). The progressive lowering of A.R. in the downstream samples records the increased influence of ground water inputs to the stream. The most uraniferous waters ($>25 \mu\text{g l}^{-1}$) showed the least variability in A.R. despite a range of over $2 \times$ in U concentration. This indicates buffering by an end-member isotopic composition of A.R. near 1.26 that is interpreted to represent *natural* U leached from local rock and soil surfaces by surface and ground water. Major contamination of these uraniferous waters with fertilizer-derived U of A.R. = 1.0 should define an apparent mixing line terminating near A.R. = 1, whereas lesser contamination should produce additional scatter of points in the area below the apparent mixing line plotted in Fig. 6.

Soil column experiment

The soil column experiment was designed to determine the relative mobility of U and other

fertilizer constituents in a column of local soil, at a controlled set of conditions. The experiment simulated local conditions by utilizing local soil, fertilizer and irrigation water, but the additional imposed conditions of uniform soil texture, continuous water saturation and uniform flow rate clearly do not duplicate the variety of these conditions operative in natural soils. Water-saturated conditions most analogous to this experimental design are only transiently attained in the study area in periodically flooded soils or in subsurface soils located near the water table. Interpretations of quantitative results such as rate of leaching or leachate composition are, therefore, qualified.

The concentrations of dissolved NH_3 , PO_4 and U in the 60 eluant fractions showed considerable variation over the course of the experiment and are plotted in Fig. 7. Other measured parameters were much less variable and showed no apparent trends over time. The specific conductance of all fractions ranged between 2700 and $3200 \mu\text{S cm}^{-1}$ compared to a value of $420 \mu\text{S cm}^{-1}$ in BDW. Dissolved SO_4 was $1400\text{--}1900 \text{ mg l}^{-1}$ compared to 95 mg l^{-1} in BDW. Dissolved Cl was $4.6\text{--}7.4 \text{ mg l}^{-1}$ compared to 7.5 mg l^{-1} in BDW. Dissolved NO_3 was generally below the detection limit of 0.1 mg l^{-1} , probably because water-saturated conditions limited the activity of nitrifying bacteria.

The elution curves for NH_3 and PO_4 showed very similar patterns of variability. Sharp peaks in the elution curves of both constituents between fractions 13 to 19 represent 'breakthrough' of the first fertilizer constituents to pass the length of the column. If breakthrough fractions are assumed to carry a soluble portion of fertilizer constituents that are largely conserved, i.e. unretarded by sorptive uptake, this indicates a column pore volume of approximately 260 ml (13 fractions \times 20 ml fraction $^{-1}$). This pore volume is approximately 40% of the saturated soil

Table 4. Uranium concentration and U isotopic composition of waters from the Sixmile Creek drainage collected August, 1993, and in 10-34-0 liquid fertilizer and soil column leachates

Sample	U ($\mu\text{g l}^{-1}$)	$^{234}\text{U}/^{238}\text{U}$ Activity Ratio	Comments
Bessemer ditch	3.1 ± 0.1	1.55 ± 0.02	SM-1 revisited
Sixmile Creek above Slough	4.5 ± 0.1	1.41 ± 0.02	SM-2 revisited
Sixmile Creek below Slough	10.9 ± 0.2	1.38 ± 0.02	SM-3 revisited
Seep near site SM-3	34.0 ± 0.4	1.38 ± 0.01	SM-3A revisited
Sixmile Creek at Olson Rd	41.6 ± 0.5	1.29 ± 0.01	SM-7 revisited
Sixmile Creek at South Rd	38.1 ± 0.4	1.29 ± 0.01	SM-8 revisited
Spring 1 at Stealey Ranch	39.9 ± 0.6	1.29 ± 0.01	SM-9 revisited
Spring 2 at Stealey Ranch	68.5 ± 0.8	1.26 ± 0.01	SM-12 revisited
Pond Outlet	$25.8 \pm 0.4^*$	1.29 ± 0.01	SM-14 revisited
Sixmile Creek at Hwy 50	$17.3 \pm 0.4^*$	1.33 ± 0.01	SM-15 revisited
10-34-0 liquid fertilizer	100 000	1.01 ± 0.03	Sampled 4/93
10-34-0 liquid fertilizer	33 800	1.00 ± 0.01	Sampled 8/93
Soil column leachate	98.6 ± 1.3	1.26 ± 0.01	Composite of fractions 1-12
Soil column leachate	48.9 ± 0.5	1.24 ± 0.01	Composite of fractions 13-50

* Concentration values lower than expected because of heavy rains the night before collection.

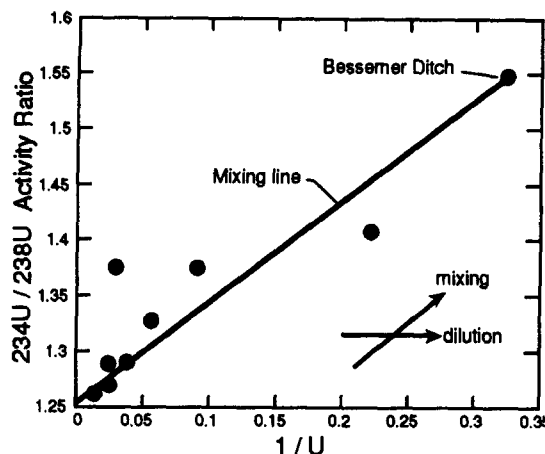


Fig. 6. Uranium isotopic composition plotted versus the reciprocal of U concentration for water samples from the drainage of Sixmile Creek. On this diagram samples that approximate two-component mixtures lie along a sloped straight-line array connecting endmember components. Vertical errors are approximately equal to the diameter of dots.

volume, which is reasonable for freshly packed fine-grained soil. This suggests that elution was not severely accelerated by channeling along selected pathways in the soil column or along the contacts between soil and container walls. In eluant fractions 19–60 both constituents continued to show sympathetic patterns of fluctuations in concentration.

The concentration of NH_3 in leachates was generally much greater than PO_4 , and, unlike PO_4 , NH_3 was progressively more concentrated in later fractions. Apparent differences in leachability relate to different mechanisms of fixation by soil particles. Ammonium ion (NH_4^+) is readily exchanged for other loosely bound cations occupying ion-exchange sites on clay minerals. In alkaline soils phosphate is fixed as relatively insoluble precipitates with Ca (Buckman and Brady, 1972). Both of these added fertilizer constituents showed strong net preference for the solid phase. The total amounts of leached NH_3 -N

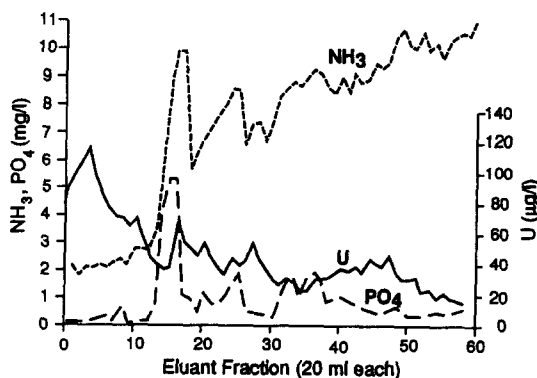


Fig. 7. Concentrations of U, NH_3 and PO_4 in successive fractions of eluant from a column of water-saturated soil, Sixmile drainage.

and PO_4 -P were approximately 4% and 0.2% of their respective amounts in 1 ml of added liquid fertilizer.

The elution curve for U differed markedly from that of NH_3 or PO_4 . The highest concentrations of U were present in the earliest fractions (1–12) prior to the breakthrough of NH_3 and PO_4 . Concentration variations of U in later fractions (13–60) did not parallel those of NH_3 and PO_4 . Uranium concentrations in the eluted fractions ranged from 130 – $20 \mu\text{g l}^{-1}$, and averaged $53 \mu\text{g l}^{-1}$; the latter value is similar to concentrations measured in water from lower portions of the Sixmile drainage (Tables 1, 2 and 4). The total amount of U contained in fractions 13–60 was approximately 40% of that contained in 1 ml of liquid fertilizer ($\text{U} = 100 \mu\text{g ml}^{-1}$) or <1% of that contained in the 1200 g of soil ($\text{U} = 5 \mu\text{g g}^{-1}$, see below).

The U isotopic compositions of composited fractions (1–12) and (13–60) were compared to look for evidence in the later fractions of the addition of fertilizer U of distinctive A.R. = 1.0. Both composites had analytically indistinguishable $^{234}\text{U}/^{238}\text{U}$ alpha activity ratios of approximately 1.24 (Table 4). This value is similar to the values of 1.26–1.29 that were consistently observed in the most uraniferous water samples in Sixmile Creek drainage (Fig. 6).

Depthwise measurements of U in recovered intervals of the soil column indicated a U concentration of $9 \mu\text{g g}^{-1}$ in the uppermost 0.25 cm compared to values of 4.9 – $5.4 \mu\text{g g}^{-1}$ in lower intervals (Fig. 8). This enrichment was selective for U compared to geochemically similar Th. The $3.5 \mu\text{g g}^{-1}$ of apparent 'excess' U in the uppermost 0.25 cm (30 g) of the soil column accounted for approximately 105% of the $100 \mu\text{g U}$ added in 1 ml of liquid fertilizer.

Other experiments

Results of the soil column experiment suggest that much of the soluble U was derived by leaching of soil particles and that U added with liquid fertilizer was largely retained in the soil. This conclusion is consistent with the results of the spatial-chemical and U-isotopic analyses of waters of Sixmile drainage. Other experimental data lent additional support to this conclusion.

A white flocculent precipitate was observed coating soil particles in the uppermost layer of the soil column, and some experiments were performed to induce formation of a similar precipitate in the absence of soil matrix. One milliliter of 10-34-0 liquid fertilizer was added to 20 ml of BDW or dilute (<0.1 M) solutions of a variety of simple salts. A white flocculent precipitate formed in solutions of CaCl_2 , MgCl_2 and CaSO_4 ; the latter generated by equilibrating BDW with crystals of gypsum. Precipitates were not observed in solutions of NaCl , Na_2SO_4 , BDW, or a solution of BDW mixed with CaCO_3 . The results suggest that threshold concentrations of dissolved Ca or Mg were needed to induce formation of the

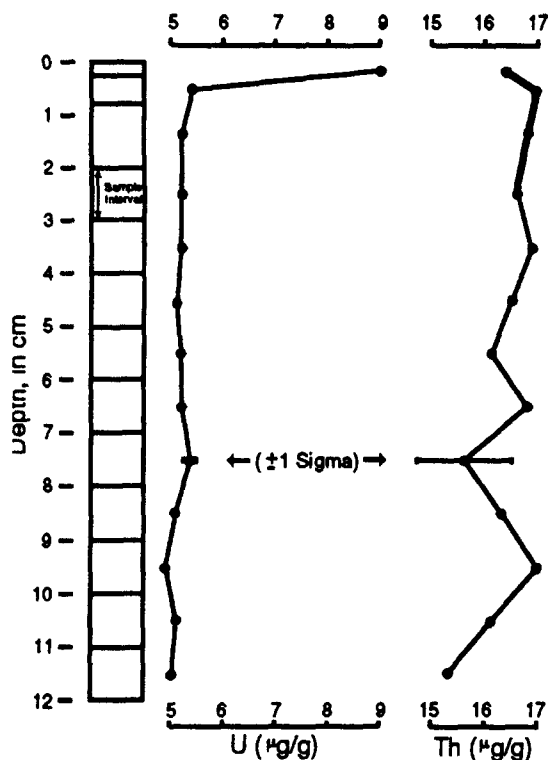


Fig. 8. Concentration of U and Th in soil layers at the end of the soil column experiment. Each plotted concentration is for a composite collected over the indicated depth interval. Horizontal bars indicate the analytical precision for U and Th.

precipitate and that at least one known constituent of local soils, i.e., gypsum, was capable of providing sufficient Ca.

A larger batch of the white precipitate was generated from gypsum-saturated BDW and further characterized. The precipitate was amorphous to X-rays and contained approximately 20 wt. % of both Ca and P as major constituents. Other major constituents (in wt. %) included N (2.2), H (2.3), Al (1.9), and Fe (1.0). A tentative identification of this precipitate was based on the results of Lindsay *et al.* (1962) who reacted ammoniated superphosphoric acid (11-33-0) with a variety of soils and soil minerals including gypsum, calcite and MgO, and identified aged precipitates to be Ca or Mg-ammonium-pyrophosphates. Other trace constituents identified in the amorphous precipitate (in $\mu\text{g g}^{-1}$) included Cr (2600), Zn (1500), Y (1000), Sr (600), Cd (500), Mn (500) and U (200). The apparent coprecipitation of U in relatively insoluble Ca-P precipitates provided a mechanism for limiting the mobility of fertilizer-derived U in the soil experiment, and perhaps in local soils.

ADDITIONAL DISCUSSION

The experimental results indicated that mobility of fertilizer-derived U was hindered by the formation of

a Ca-P-U precipitate that formed by reaction of P-bearing fertilizer solution with soluble Ca in soil porewater. The most likely source of soluble Ca in the soils of Sixmile drainage is gypsum. In highly irrigated soils of the drainage most of the gypsum and other soluble salts are leached from the plow layer. This was confirmed by reconnaissance sampling and partial analysis (U and anions) of surface runoff from irrigated fields. Surface runoff was little changed in specific conductance and chemistry compared to applied BDW. This suggests that, unlike the soil column results, Ca-P-U precipitate formation may occur over a deeper and more diffuse zone in irrigated soils. This greater dispersion of Ca-P-U precipitate in larger volumes of soil and the periodic mixing of upper layers of soil by tillage explains why analysis of bulk soil is a poor indicator of U enrichment from fertilizer. Previous attempts to isolate and characterize rare P-rich particles from highly fertilized soils have met with limited success (Pierzynski *et al.*, 1990).

The composition and crystallinity of P-rich precipitates is a function of the type of soil and the type of applied fertilizer (Lindsay *et al.*, 1962) and this probably influences uptake and retention of U. In acid soils, Al-P or Fe-P precipitates form instead of Ca-P precipitates (Buckman and Brady, 1972). Precipitation of Al-P or Fe-P compounds from mixtures of acid soil and 10-34-0 liquid fertilizer is hindered by the strong complexing of Al and Fe with pyrophosphate (Lindsay *et al.*, 1962). If amorphous Ca-P precipitates form in fertilized soils of Sixmile Creek drainage they probably undergo further modification during prolonged residence in soil, with unknown effects on contained U. The data of Lindsay *et al.* (1962) suggest that the amorphous precipitate should initially age to a crystalline compound of Ca-ammonium-pyrophosphate. Pyrophosphate slowly hydrolyses to orthophosphate in the soil environment, leading to eventual formation of relatively insoluble monetite (CaHPO_4) or apatite (Buckman and Brady, 1972). The fate of U during these conversions is unknown but crystalline apatite is a common mineral host for U.

CONCLUSIONS

High concentrations of dissolved uranium in the intensively cultivated drainage of Sixmile Creek, southeastern Colorado, are the result of natural or irrigation-enhanced leaching of local soils rather than contamination with fertilizer-U. This conclusion is based on: (1) Synoptic sampling of Sixmile Creek, with particular attention to the decoupled build-up of dissolved U and dissolved NO_3 ; (2) U isotopic measurements of sampled waters that limited the possible contribution from isotopically distinct U contained in fertilizer; (3) Experimental leaching studies that documented the immobility of fertilizer-U in local soils using a combination of chemical and

U-isotopic data; and (4) Identification and characterization of a Ca-P-U precipitate that formed in soil and that efficiently sequestered U added with fertilizer solution.

The investigative methods employed in this study have application to other agricultural areas where fertilizer is suspected to contribute dissolved U to local waters. Similar studies are needed elsewhere because the mobility of fertilizer-U in soils and the nature of P and U-rich precipitates will vary depending on soil properties (pH, moisture, mineralogy, texture), pore-water chemistry, and type of applied fertilizer. Studies of agricultural practices such as fertilization that can influence dissolved U are critical for defining best-management practices that sustain crop yields while minimizing U contamination of irrigation drainage. Uranium is a ubiquitous component of soils and phosphate-based fertilizer and the concern for non-point-sources of U will increase with the enactment of drinking water quality standards for U.

Acknowledgements—We extend special thanks to Mr and Mrs F. G. Thacker, and Mrs G. Centa for providing access to their property for collection of water and soil samples, and for assisting in periodic collection of tailwater samples. Mr P. R. Stealey was very helpful in providing access to several springs. Mr M. C. Genova of American Fertilizer Company graciously provided samples of 10-34-0 fertilizer and other local fertilizers. Mr T. Broz of Kugler Corp. provided information on the origin and production of 10-34-0 liquid fertilizer. T. F. Kraemer of the USGS provided much information on previous studies of U in fertilizer and fertilized soils. J. K. Böhlke of the USGS provided critical advice regarding analyses of nitrogen isotopes. Other USGS personnel who provided analytical help included P. H. Briggs, K. J. Esposito, R. J. Knight, M. J. Malcolm, C. T. Pierson, C. L. Skeen, G. L. Skipp, and R. B. Wanty.

Editorial Handling: Dr Ron Fuge.

REFERENCES

- Abbott P. O. (1985) Description of water systems operations in the Arkansas River basin, Colorado, *U.S. Geol. Surv. Water-Res. Invest. Rep.* 85-4092.
- Alley W. M. (1993) Regional Ground-Water Quality, Van Nostrand Reinhold.
- Barisic D., Lulic L. and Miletic P. (1992) Radium and uranium in phosphate fertilizers and their impact on the radioactivity of waters. *Water Res.* 26, 607-611.
- Buckman H. O. and Brady N. C. (1972) The Nature and Properties of Soils, seventh edition, Macmillan Company.
- Cain D. (1985) Quality of the Arkansas River and irrigation-return flows in the lower Arkansas River valley, Colorado, *U.S. Geol. Surv. Water-Res. Invest. Rep.* 84-4273.
- Cain D. and Edelman P. (1980) Selected hydrologic data, Arkansas River basin, Pueblo and southeastern Fremont Counties, Colorado, 1975-1980, *U.S. Geol. Surv. Open-File Rep.* 80-1185.
- Guimond R. J. and Windham S. T. (1975) Radioactivity distribution in phosphate products, by-products, effluents, and wastes. *U.S. Environmental Protection Agency, Office of Radiation Programs, Technical Note ORP/CSD-75-3*.
- Hach Company (1992) *Water Analysis Handbook*, 2nd Edition, Hach Company, Loveland, CO.
- Heaton T. H. E. (1986) Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: a review. *Chem. Geol.* 59, 87-102.
- Johnson C. A., Zielinski R. A. and Asher-Bolinder S. (1995) Nitrogen isotopes in nitrate from surface waters and shallow ground waters at Sixmile Creek, southeastern Colorado, *U.S. Geol. Surv. Open-File Rept.* 95-536.
- Kendall C. and Grim E. (1990) Combustion tube method for measurement of nitrogen isotope ratios using calcium oxide for total removal of carbon dioxide and water. *Analyt. Chem.* 62, 526-529.
- Kuroda P. K., Burchfield L. A. and Essien I. O. (1989) Thorium, uranium and plutonium isotopes in the Arkansas River. *J. Radioanal. and Nucl. Chem.* 131, 369-375.
- Langmuir D. (1978) Uranium solution-mineral equilibria at low temperatures with application to sedimentary ore deposits. *Geochim. Cosmochim. Acta* 42, 547-569.
- Larsen R. J., Wiggins T. J., Holden D. L., McCulloch M. B. and Preator R. E. (1979) Soil survey of Pueblo area, Colorado; parts of Pueblo and Custer Counties. *U.S. Dept. of Agriculture, Soil Conservation Service*.
- Lindsay W. L., Frazier A. W. and Stephenson H. F. (1962) Identification of reaction products from phosphate fertilizers in soils. *Soil Sci. Am. Proc.* 26, 446-452.
- Madison R. J. and Brunett J. O. (1985) Overview of the occurrence of nitrate in ground water of the United States. In *National Water Summary 1984—Hydrologic events, selected water quality trends and ground-water resources* *U.S. Geol. Surv. Water-Supp. Paper* 2275, 93-105.
- Mangini A., Sonntag C., Bertsch G. and Muller E. (1979) Evidence for a higher natural uranium content in world rivers. *Nature* 278, 337-339.
- McKelvey V. E. and Carswell L. D. (1956) Uranium in the Phosphoria Formation. In *Contributions to the Geology of Uranium and Thorium by the U.S. Geological Survey and the Atomic Energy Commission for the United Nations International Conference on Peaceful Uses of Atomic Energy, Geneva, Switzerland, 1955* (eds. L. R. Page, H. E. Stocking and H. B. Smith), *U.S. Geol. Surv. Prof. Paper*, 300, pp. 477-482.
- Meline R. S., Lee R. G. and Scott W. C. (1972) Use of a pipe reactor in production of liquid fertilizers with very high polyphosphate content. *Fertilizer Solutions Magazine*, March-April.
- Menzel R. G. (1968) Uranium, radium, and thorium content in phosphate rocks and their possible radiation hazard. *J. Agric. Food Chem.* 16, 231-234.
- Millard H. T. and Keaten B. A. (1982) Precision of uranium and thorium determinations by delayed neutron counting. *J. Radioanal. Chem.* 72, 489-500.
- Mueller D. K., DeWeese L. R., Garner A. J. and Spruill T. B. (1991) Reconnaissance investigation of water quality, bottom sediment, and biota associated with irrigation drainage in the middle Arkansas River basin, Colorado and Kansas, 1988, *U.S. Geol. Surv. Water-Res. Invest. Rep.*, 91-4060.
- Osmond J. K. and Cowart J. B. (1982) Ground water. In *Uranium Series Disequilibrium: Applications to Environmental Problems* (eds M. Ivanovich & R. S. Harmon), 202-245, Clarendon Press.
- Parkhurst D. L., Thorstenson D. C. and Plummer L. N. (1980) PHREEQE—a computer program for geochemical calculations, *U.S. Geol. Surv. Water-Res. Invest. Rep.*, 80-96.
- Pierzynski G. M., Logan T. J., Traina S. J. and Bigham J. M. (1990) Phosphorous chemistry and mineralogy in excessively fertilized soils: quantitative analysis of phosphorous-rich particles. *J. Soil Sci. Soc. Am.* 54, 1576-1595.
- Rössler C. E., Smith Z. A., Bolch W. E. and Prince R. J. (1979) Uranium and radium-226 in Florida phosphate materials. *Health Phys.* 37, 269-277.

- Rosholt J. N. (1984) Radioisotope dilution analysis of geological samples using ^{236}U and ^{229}Th . *Nucl. Instrum. Methods* **223**, 572–576.
- Rothbaum H. P., McGaveston D. A., Wall T., Johnston A. E. and Mattingly G. E. G. (1979) Uranium accumulation in soils from long-continued applications of superphosphate. *J. Soil Sci.* **30**, 147–153.
- Scott M. R. (1982) The chemistry of U and Th series radionuclides in rivers. In *Uranium Series Disequilibrium: Applications to Environmental Problems* (eds M. Ivanovich and R. S. Harmon), Clarendon Press, pp. 181–201.
- Scott G. R., Taylor R. B., Epis R. C. and Wobus R. A. (1978) Geologic map of the Pueblo 1° X 2° quadrangle south-central Colorado. *U.S. Geol. Surv. Map I-1022*, scale 1:250 000.
- Spalding R. F. and Exner M. E. (1993) Occurrence of nitrate in groundwater—a review. *J. Environ. Qual.* **22**, 392–402.
- Spalding R. F. and Sackett W. M. (1972) Uranium in runoff from the Gulf of Mexico distributive province: anomalous concentrations. *Science* **175**, 629–631.
- Taylor S. R. and McClelland S. M. (1985) *The Continental Crust: its Composition and Evolution*. Blackwell Scientific.
- Trudell M. R., Gilliam R. W. and Cherry R. A. (1986) An in-situ study of the occurrence and rate of denitrification in a shallow unconfined sand aquifer. *J. Hydrol.* **83**, 251–268.
- U.S. Department of Commerce (1991) National Climatic Data Center Climatological Data Annual Summary, Colorado. Vol 96, no. 13, 1991, ISSN 0145-0506.
- U.S. Environmental Protection Agency (1991) National primary drinking water regulations for radionuclides, proposed rule, June, 1991. Washington, D.C., Office of Ground Water and Drinking Water, EPA Fact Sheet, Radionuclides in Drinking Water, 570/9-71-700.
- World Health Organization (1993) Guidelines for Drinking Water Quality. WHO Publications, Geneva.
- Wrenn M. E., Durbin P. W., Willis D. W. and Singh N. P. (1987) The potential toxicity of uranium in water. *Am. Water Works Ass. J.* **79**, 177–184.
- Zielinski R. A., Asher-Bolinder S. and Meier A. L. (1995) Uraniferous waters of the Arkansas River valley, Colorado, U.S.A.: a function of geology and land use. *Appl. Geochem.* **10**, 133–144.